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On the Process of Photo-induced Desorption of Sodium Atoms from Polydimethylsiloxane Films

Werner F. Schmidt[1,2], Eugen Illenberger[1], and Katsumi Yoshino[2]
[1]Research Group Illenberger, Institute of Physical Chemistry, Freie Universität Berlin, Germany
[2]Department of Electronic Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka, 565-0871, Japan

A few years ago, an unusual photodesorption phenomenon involving alkali atoms on polymeric films of polydimethylsiloxane (PDMS) was reported. A film of PDMS exposed to sodium vapor absorbs the alkali atoms. Illumination of this loaded film with visible light leads to an increase of concentration of sodium atoms in the vapor space above the film [1].

This photodesorption mechanism seems to be unique for PDMS films since it has not been found for other films of parafins or crown ethers. A spectroscopic study of the frequency dependence of the effect yielded for the desorption of Na a threshold value of $1/\lambda = 9500\ cm^{-1}$ and for the desorption of Na_2 a threshold value of $11500\ cm^{-1}$. It was assumed that a charge transfer complex between the sodium and the PDMS was formed [2]. New experiments on the temperature dependence of the effect yielded activation energies of 0.36 eV and 0.34 eV, respectively, which the authors attribute to the diffusion process at the surface [3]. While the kinetics of the desorption process could be described satisfactorily [4,5], the energetics of the process remained in question.

Here we wish to discuss some of the physical factors which have to be taken into account in the development of a physically reasonable model.

Some years ago we measured the energy of the delocalized electron level of various silicone oils by photoemission [6]. The different dimethylsiloxanes gave values of V_0 between - 0.87 eV and - 0.77 eV. This is in stark contrast to values around zero for n-alkanes [7]. Obviously the local Si-O microdipoles play an important role. The energetic condictions are depicted in Fig. 1. When the sodium atom approaches the surface, a slight separation of charges takes place in the sense that the lone valence electron is attracted by the conduction level of the PDMS while the positive charge induces an attractive polarization in the PDMS. For a medium with a dielectric constant of 2 the polarization energy according to Born's formula [7] is given as

$$P_+ = - 3.6/R(Å) \quad \text{in eV}$$

If the sodium ion penetrates completely into the bulk, its polarization energy amounts to about - 1.9 eV. Here, we took the hard core radius of Neon as that of the ion. Together with V_0 a reduction of the gas phase ionization energy of sodium of - 2.7 eV results. We have to assume that in addition electron traps exist in this material. Extrapolationg from the optical absorption of

localized electrons in liquid n-alkanes [7] the trapping energy should be between 1 and 2 eV in PDMS. When the sodium atom approaches the surface, the lone electron transfers into such a trap while the positive ion is attracted into the bulk of the film. Both species are trapped in close spacial correlation. In the desorption process the localized electrons absorb the visible light and transfer back to the sodium ion. The neutral sodium atom then - due to the contration gradient - diffuses out of the film. It is possible that the formation and destruction of such charge transfer complex takes place several times during the diffusion towards the surface.

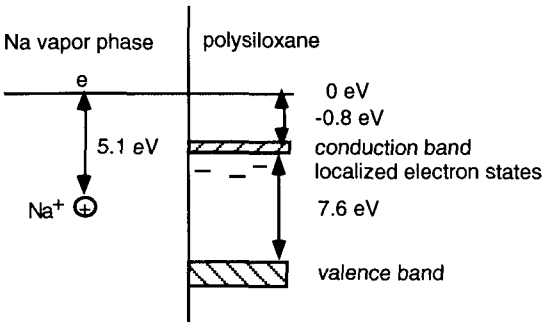

Fig. 1: Energetic conditions

This process of light enhanced desorption of sodium atoms (the process was found also for other alkali atoms) might lead to some application in such a manner that a certain pattern of illumination might be converted at the surface of the film into a corresponding pattern of desorbed alkali atoms which then by some chemical reaction have to be fixated.

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